Electrochimica Acta 188 (2016) 653–660

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Iron vs Aluminum Based Layered Double Hydroxides as Water Splitting Catalysts

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ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 9 November 2015
Accepted 7 December 2015
Available online 10 December 2015

Keywords:
OER
Layered Double Hydroxides
glassy carbon
platinum
electrosynthesis

ABSTRACT

This paper describes the electrosynthesis, characterization and electrocatalytic properties towards oxygen evolution reaction (OER) of four layered double hydroxides (LDHs) containing cobalt or nickel as divalent cation and aluminum or iron as trivalent metal. The electrochemical behaviour of the LDH modified electrodes was studied by cyclic voltammetry (CV), and the LDHs were characterized by XRD and SEM/EDS. Two materials, *i.e.*, platinum and glassy carbon (GC), were investigated as electrode supports recording polarization and chronopotentiometric curves, with a rotating disk electrode in alkaline solutions. LDHs containing iron exhibited higher activity for OER and all the materials showed a good stability and durability in alkaline media. When GC was used as electrode support the performances of the OER catalysts resulted to be even better than those exhibited by the same LDHs electrodeposited on Pt.

1. Introduction

At present, there is intense research for new highly efficient and low cost catalytic systems in the field of global energy issues. Efficient electrocatalysts for oxygen evolution reaction (OER) represent a critical component in various energy devices, such as solar cells, metal–air batteries [1] and hydrogen generation from water splitting [2]. OER is the process of generating molecular oxygen through the electrochemical oxidation of water. The main problem of the OER is the slow kinetics due to its multistep proton-coupled electron transfer process, so the electrolysis requires a relatively high potential if compared with the standard potential (+1.23 V) for water-splitting. An effective electrocatalyst is needed in order to expedite the reaction, reduce the overpotential and enhance the energy conversion efficiency. Currently, precious metal oxide catalysts like iridium oxide (IrO_2) and ruthenium oxide (RuO_2) are the best known OER electrocatalysts [3–5] but their applications are restrained because of their excessive cost and scarcity. Therefore, it is critical to find highly efficient alternative catalysts which offer large scale availability and which are also able to enhance catalytic performance for OER applications. Extensive efforts have been undertaken to develop active and low cost alternative such as hybrid materials obtained by anchoring inorganic nanomaterials on oxidised carbon substrates [6] first-row transition metals oxides containing nickel, cobalt, vanadium and manganese [7,8] and perovskites [9]. Layered double hydroxides (LDHs) are very promising materials for a large number of possible applications due to their versatility, tunable properties, wide range of compositions and low cost. Recently, LDH materials have been also proposed as OER catalysts [10,11]. LDHs are lamellar compounds, with the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A_n{}^{x-}{}_{x/n})\cdot mH_2O$, where M(II) and M(II) represent the divalent and trivalent cations, respectively, A_n is an n-valent anion, and x ranges usually between 0.2 and 0.5. Their structure consists of positively charged brucite-like layers and the positive charge is balanced by the presence of interlayer anions. For this reason they are also called anionic clays. These materials can be used as electrode modifiers and the electrodeposition of LDHs allows the simultaneous synthesis and modification of the electrode surface [12]. The method is based on the electrochemical production of hydroxide anions necessary to induce the LDH precipitation on the electrode surface by cathodic reduction of nitrate ions [13]. Recently, LDHs are attracting much interest in the area of electrochemistry for applications such as batteries, supercapacitors, sensors, and fuel cells [14,15], for which the adhesion of the clay to the conductive support is a fundamental property. In the last few years our group has optimized a preliminary treatment of Pt surfaces in order to get thin film of LDHs based on Ni or Co and Al, which resulted well adhered to the conductive support [16,17].

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http://dx.doi.org/10.1016/j.electacta.2015.12.059
0013-4686/

In this work we studied the OER catalytic activity of four LDHs containing Co or Ni as divalent metal and Al or Fe as trivalent one with the aim to investigate the effect of the substitution of Al with Fe. Any conductive material can be easily modified with LDHs film obtained by electrosynthesis. On the basis of our experience on Pt the study was at first carried out using this support. Later also glassy carbon (GC) was taken into account since most of the papers dealing with the OER activity of catalysts employ GC as electrode material, which is also inexpensive in respect to platinum [10,18]. Therefore, a comparison of the OER activity of the tested Fe and Al based catalysts grown on Pt and GC was made and the results were that their performances are little dependent on the kind of support.

2. Experimental

2.1. Apparatus

The electrochemical deposition and characterization were performed by using a PGSTAT 20 Autolab potentiostat (Ecochemie) controlled by a personal computer via GPES 4.9 software (Windows operating system) and by using a CH Instrument Mod. 660C, controlled by a personal computer via CH Instrument software.

All electrochemical experiments were carried out using a single compartment, three-electrode cell. A Pt or GC rotating disk electrode (RDE, 0.5 mm diameter) was employed as working electrode, using a PINE Research Instrumentation Modulated Speed Rotator (MSR). A platinum wire (Sigma Aldrich) was used as counter electrode, a saturated calomel electrode (SCE) as reference one when the electrochemical pre-treatment of the electrodes and the deposition of the LDHs were carried out, while a Hg/HgO electrode was used as reference electrode when performing all the characterizations. Both electrodes were purchased from Amel Instruments.

The morphology and the chemical compositions of LDH films were investigated by Field Emission-Scanning Electron Microscopy (FE-SEM) LEO 1525 ZEISS instrument fitted with an EDS detector, working with an acceleration voltage of 15 kV.

X-ray diffraction patterns were obtained with CuKα radiation in reflection mode by means of an X'Pert PANalytical diffractometer equipped with a fast X' Celerator detector: 0.06° step, 200s/step. The samples were analyzed directly putting the Pt electrode in the optical centre of the diffractometer.

2.2. Chemicals

Cobalt(II) nitrate hexahydrate (98% pure), nickel(II) nitrate hexahydrate (99.999%), aluminum nitrate nonahydrate (>96%) and sodium hydroxide (98%) were supplied by Sigma-Aldrich. Iron(III) nitrate nonahydrate (99% pure) and sulfuric acid (95-98% w/w) were purchased from Riedel-de Haën and J. T. Backer, respectively.

The supporting electrolyte for all the electrochemical experiments was NaOH at two different concentrations, 0.1 and 1 mol/L. The salt solutions were prepared with doubly distilled water.

2.3. Pt electrode modification

Cleaning the electrode is a critical step to achieve a well adherent coating so the Pt electrodes were prepared as follows [19]. The surface was polished to a mirror-like surface first by a mechanical cleaning, using sand-paper and aqueous alumina (0.05 μm) slurry on a wet polishing cloth, and then the electrode was submitted to the following electrochemical treatment. First 250 cycles between -0.25 V and +1.30 V were performed in 0.1 M H_2SO_4 at the scan rate of 1 V s^{-1}. Afterwards the electrode was polarized at the potential of -0.90 V *vs* SCE for 300 s (under stirring in order to remove hydrogen bubbles) in 1 M H_2SO_4, followed by 3 CV cycles between -0.20 V and +1.30 V in 0.1 M H_2SO_4. The LDH films were deposited on the electrode surface by cathodic reduction of a freshly prepared 0.03 M solution containing M(II) and M(III) at a molar ratio of 3:1. The electrochemical reaction was carried out by applying a fixed potential (-0.90 V *vs* SCE) for 30 s. After performing the modification, the electrode was immediately rinsed with water. In order to directly record the XRD patterns of the four LDHs, the electrodeposition step was repeated 10 times at the same electrode (total deposition time of 300 s).

2.4. GC electrode modification

Even in the case of GC electrode, a mechanical treatment followed by an electrochemical cleaning was performed. The electrode surface was polished to a mirror-like surface first by a mechanical cleaning with sand-paper and aqueous alumina (0.05 μm) slurry on a wet polishing cloth. Afterwards the electrode was cycled between -0.50 V and +0.50 V in 0.1 M H_2SO_4 at the scan rate of 0.1 V s^{-1} until the cycles were superimposable. For the GC electrode the LDH films were obtained in the same conditions as those used for Pt with the only exception that the electrode was biased at -1.1 V *vs* SCE.

2.5. OER activity investigation

The OER catalytic activity of the electrodes coated with the LDHs was investigated in alkaline solution (0.1 and 1 M NaOH) by linear sweep voltammetry (LSV), recording iR-corrected polarization curves at the scan rate of 0.005 V s^{-1}. The Tafel plots were constructed using the LSV data.

The durability of the LDHs was studied recording chronopotentiometric curves by applying for an hour three different current densities: 1.5, 2.0 and 2.5 mA cm^{-2}. During both the LSV and chronopotentiometric experiments, the working electrode was constantly rotating at 1600 rpm in order to remove the oxygen bubbles from the electrode surface.

3. Results and discussion

3.1. Structural characterization of the synthesized LDHs

With the aim to verify the structure of the LDHs, X-ray diffraction (XRD) analysis has been carried out directly on the Pt-electrodes, even though the amount of the deposited material is low. The patterns of all the samples, reported in Fig. 1, show the main diffraction maximum typical of LDH phase, indexed as 003 reflection. In three samples also the 006 peak is detectable [20].

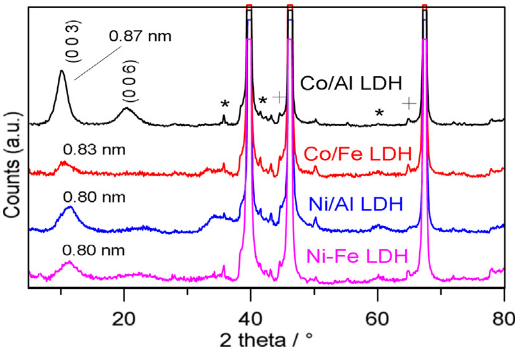

Fig. 1. XRD patterns of the LDHs electrosynthesized on Pt, instrumental background subtracted. The clipped reflections are due to Pt electrode. The asterisks and the crosses mark extra peaks (Pt peaks due to CuKβ and WLα radiation respectively) which are detectable because the very high intensity of Pt reflections.